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Influence of processing parameters on the electrical response of screen printed $SrFe_{0.6}Ti_{0.4}O_{3-\delta}$ thick films

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Abstract

A screen printing ink of $SrFe_{0.6}Ti_{0.4}O_{3-\delta}$ (STFO60) nanopowders produced by Self-propagating High-temperature Synthesis (SHS) was used to produce gas sensors with high level of reproducibility at low cost. The stability and rheology of the produced ink were studied in order to obtain high quality, highly reliable films. The electrical characteristics of the sensors as a function of the firing temperature and thickness of the sensing layer were investigated. The best results were obtained stabilizing the powder with lauric acid. Laboratory bench and on-road oxygen tests demonstrated that the response of 30 μm STFO60-based resistive sensors is comparable with the one of a commercial oxygen probe.

Keywords: $SrFe_{0.6}Ti_{0.4}O_{3-\delta}$; Oxygen sensors; Screen printing; Inks

1. Introduction

Modern combustion engines operate under lean conditions ($\lambda > 1$) [1]. To guarantee a precise engine control, fast and accurate oxygen sensors able to stand the aggressive conditions of the engine exhausts are needed. Iron doped strontium titanate ($SrFe_{0.6}Ti_{0.4}O_{3-\delta}$, STFO60) is a promising alternative to the commonly used zirconia for resistive oxygen sensors [2,3].

In order to meet the automotive industry's cost requirements, these sensors can be conveniently manufactured by screen printing. This is a simple and automated manufacturing technique that allows the production of low cost and robust chemical sensors with the required level of reproducibility leading to a general reduction of the sensors cost [4]. The technique is also compatible with the standard CMOS (Complementary Metal Oxide Semiconductor) processing and can be therefore applied for the production of fully integrated devices [5,6].

Several factors contribute to the success of producing high quality thick-film circuits, with the rheology of the thick-film paste being the most important one [7,8]. The ideal ink should have the proper degree of both pseudoplastic and thixotropic behaviour. The viscosity should remain low for a short time so that the printed film can level, filling the unevenness due to the screen wires. On the other hand, when the ink rests on the substrate, it is subjected to gravity and therefore to a very low shear rate. Under these conditions, its viscosity should quickly increase with time to prevent bleeding out of the film [9].

The key points to obtain a reliable and high performance sensors are the oxide intrinsic properties as well as an accurate manufacturing technique. Screen printing inks are complex non-equilibrium systems having flow properties strongly related to the nature and amount of their components [10]. Therefore a right blend of organic components is crucial to obtain a stable ink with suitable rheological properties.

The aim of this work was to study and optimize a screen printing ink of $SrFe_{0.6}Ti_{0.4}O_{3-\delta}$ nanopowders produced by Self-propagating High-temperature Synthesis (SHS) [11] to

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allow the production of high performance low cost gas sensors with the right level of reproducibility. Sensors with different thermal treatments and thickness of the sensing layer have been investigated and their performance compared with those of a commercial electrochemical oxygen sensor.

2. Experimental

2.1. Powder synthesis and characterization

$SrFe_{0.6}Ti_{0.4}O_{2.8}$ (STFO60) powders were prepared by the Self-propagating High-temperature Synthesis (SHS) technique and subsequent ball-milling treatment (BM) as presented elsewhere [11]. They were characterized by B.E.T. single-point method (SSA) (Sorpy 1750, Carlo Erba, Italy), X-ray diffraction (Philips PW 1830, using Ni-filtered Cu Kα radiation, $\lambda = 1.5405$ Å) and scanning electron microscopy (SEM) (HITACHI S400, Japan).

2.2. Ink preparation and characterization

Terpineol-based inks were initially prepared in agate mortar and then transferred into a three-roller grinding mill equipped with zirconia rollers of nanometric finish (Exakt 80E, Exakt, Nordestedt, Germany) to improve homogeneity. Three deflocculants were tested for the dispersion of STFO60 powder in terpineol (Fluka, Germany): (1) a polyenoic ester (glycerol trioleate (GTO), Fluka, Germany); (2) a fatty acid (lauric acid (AL), Fluka, Germany) and (3) an heterocyclic acid (furoic acid (AF), Fluka, Germany). Ethyl cellulose (EC) (Fluka, Germany) was used as binder.

Rheological behaviour of the inks was analysed using a controlled-stress rotational rheometer (Bohlin C-VOR 120, Bohlin, Malvern, UK) equipped with serrated plates (diameter = 25 mm). Measurements were performed at 298 K by setting the plates distance at 500 μm. Viscosity-shear rate measurements were performed by sweeping over 22 values of shear rates (in logarithmic scale), the minimum and maximum being 0.01 and 100 s^{-1}, respectively. For each measurement a pre-shear of 2 min at 185 s^{-1} was first applied after which the shear rate was increased and then sequentially decreased.

Thixotropy has been investigated applying a rapid change of shear rate to the inks from a steady state at high shear rate to a lower one. The starting shear rate of 100 s^{-1} was chosen to simulate flow conditions through the meshes, while the values of lower shear rates (10, 1, 0.1 and 0.01 s^{-1}) mimic its evolution with time after the passage through the mesh. These jumps were applied following the sequential pattern according to the Camina–Roffey procedure.

Zeta potential measurements were performed on suspensions of the powder in terpineol (5 vol%) using an electroacoustic spectrometer (AcoustoSizer II, Colloidal Dynamics, Warwick, RI, USA). The instrument determines the ζ-potential of particles by fitting the dynamic mobility over a range of frequencies (from 1 to 18 MHz) of an imposed electric field. The same sound attenuation technique is used to measure the particle-size distribution necessary for the fitting.

2.3. Thick-film deposition

Thick films were screen printed (squeegee speed = 0.12 m/s, squeegee load = 6.5 kgF, snap off = 0.7 mm; AUR'EL 900, AUR'EL Automation S.p.A., Italy) onto alumina substrates (6 mm × 3 mm) supplied with comb-like electrodes and a Pt heater on the backside and left to dry at room temperature in air. A suitable mask was used to print each time the sensing element on a row of the ceramic substrate containing 12 interdigited structures.

The as-deposited films were analysed through optical microscopy (Leitz DMRME, Leica, Germany) and heat-treated at temperatures between 700 and 1100 °C. The sintered film microstructure was analysed using scanning electron microscopy and the film adhesion tested with the conventional scotch test.

2.4. Oxygen sensing tests

Sensing tests were performed at 650 °C with computer-assisted equipment running on LabView platform. The resistance measurements were done maintaining the sensors under a flow of dry nitrogen (200 cc/min) while pulsing different oxygen amounts in the range 0.1–20 vol%. Further details about the sensing tests procedure can be found elsewhere [11].

3. Results and discussion

3.1. Ink preparation

STFO60 nanopowders consist of agglomerates of about 5 μm (Fig. 1) with primary particle size of 40 nm, as calculated from XRD analysis. The specific surface area (SSA) corresponding to this particle dimension is 35.6 m^2/g [12]. The value is notably higher than the one obtained through nitrogen absorption (2.38 m^2/g). This effect is probably due to the agglomeration of the powder during the SHS process. The formulation of an ink with sub-micrometric powders is complicated by the large quantity of organics needed to ensure the desired rheology [13]. This high level of organics can easily lead to cracks during the heat treatment.

In order to obtain a stable and homogeneous ink, it is very important to effectively disperse the ceramic particles in the organic solvent (terpineol). The stability of the suspension depends on the effectiveness of the dispersant. The particles can be stabilized via one or a combination of two mechanisms: electrostatic repulsion or steric stabilization [14]. Among the three dispersant chosen, Glycerol Trioleate (GTO) is purely steric, furoic acid (AF) is purely electrostatic and lauric acid (AL) possesses a combination of electrostatic and steric activity. In order to find the most effective dispersant for the STFO60 system, sedimentation tests and zeta potential measurements were made. The sedimentation test can help to evaluate the efficiency of the dispersant with steric activity while the zeta potential analysis is used to test the performance of the electrostatic one. In the sedimentation test, the